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The Effect of Surface Pressure on Langmuir-Blodgett Polymerization of 2-Pentadecyl Aniline

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by

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In this paper the effect of applied surface pressure upon the Langmuir-Blodgett polymerization of 2-pentadecyl aniline is investigated. Increasing the surface pressure was found to increase the polymerization rate dramatically. Experiments were performed to elucidate the underlying cause of this effect.

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THE EFFECT OF SURFACE PRESSURE ON THE LANGMUIR-BLODGETT POLYMERIZATION OF 2- PENTADECYL ANILINE

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INTRODUCTION

In recent years there has been a renewed interest in Langmuir-Blodgett (L-B) films due to the improved non-linear optical and electronic characteristics shown by polymeric L-B films (1,2). Consequently, there have also been significant advances in L-B instruments, yet many studies continue to use the L-B technique uniquely as a method to prepare multilayer films. Our laboratory is interested in preparing L-B multilayers, while also using the technique as a probe to study polymerization reactions restricted to two dimensions. This paper will discuss the polymerization of a functionalized polyaniline.

Polyaniline can be made by both chemical and electrochemical polymerization techniques(3,4). The polymerization is usually conceded to proceed by oxidative coupling, yet the detailed mechanism remains unclear(5). We have shown previously that 2-pentadecyl aniline can be chemically polymerized on a L-B trough (6,7). It was also shown that the change in the mean molecular area of the molecules at the air/aqueous interface could be used as a method to observe the polymerization process as it happens in a manner analogous to classical dilatometry of bulk polymerizations. During the polymerization of 2-pentadecyl aniline the mean molecular area was observed to decrease from 40-50 $Å^2$ to a constant value of approximately 20-30 $Å^2$ (depending on the applied surface pressure) as the polymerization was finished. The following text will discuss the effect of the applied surface pressure on this L-B polymerization.

EXPERIMENTAL

Solutions for spreading were made by dissolving the monomer, 2-pentadecyl aniline, and stearic acid(TCI) in spectra grade chloroform(Kodak). The solutions of sulfuric acid and ammonium peroxydi- sulfate were prepared with Milli-Q® water. Experiments were performed on a customized KSV 5000 L-B system. All polymerizations were made by spreading the monomer in dilute chloroform solution on an aqueous subphase of 0.5M sulfuric acid and 0.05M ammonium peroxydisulfate. Figure 1 shows a typical surface pressure vs surface area isotherm for 2-pentadecyl aniline on the subphase of 0.5M sulfuric acid. After spreading, the monomer was then quickly compressed to the desired surface pressure for the polymerization and the surface pressure was maintained constant by changing the barrier position as necessary. The instantaneous barrier speed, mean molecular area, and surface pressure were all then recorded as a function of time during the polymerization. Zero time was defined to be when the desired surface pressure was reached.

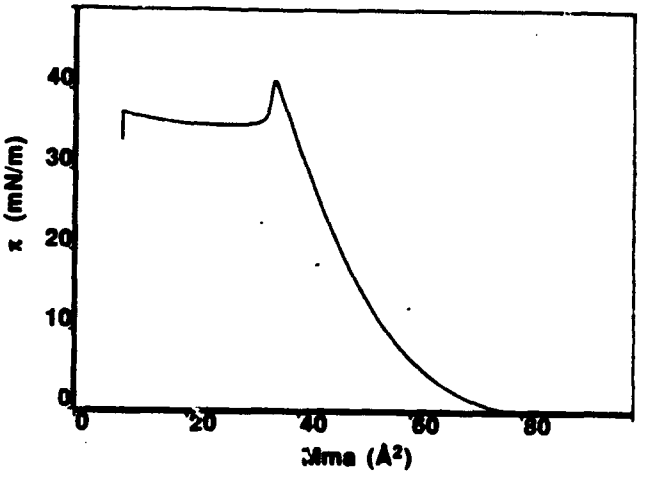

FIGURE 1. Surface pressure (π) vs mean molecular area (Mma) isotherm of 2-pentadecyl aniline on a 0.5 M H_2SO_4 subphase.

RESULTS AND DISCUSSION

Mean molecular area vs time isobars for the polymerization of 2-pentadecyl aniline under different applied surface pressures are shown in Figure 2. This figure shows that the mean molecular area decreased as a function of time during the polymerization for all surface pressures. The polymerization was completed when the mean molecular area reached a constant value. The differences in the mean molecular areas at the end of the polymerization are largely due to the polymer

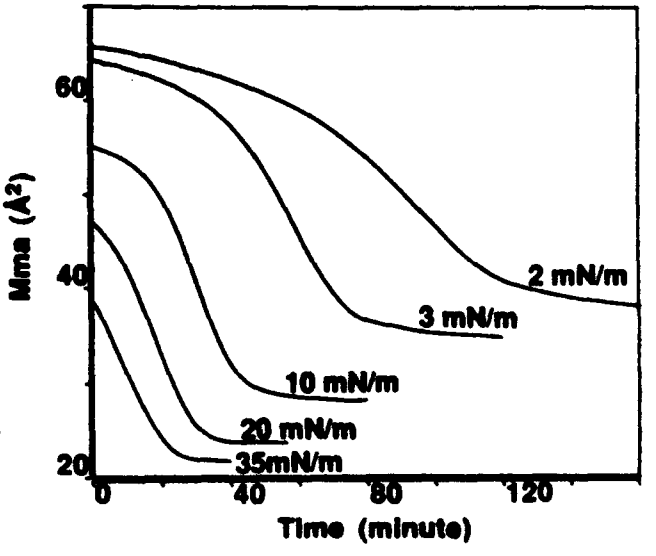

FIGURE 2. The mean molecular area (Mma) vs reaction time at different applied surface pressures during the polymerization.